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(54) Hydrotreating process.

(57) A hydrotreating process comprising:

(i) further hydrotreating partly hydrotreated hydrocarbon oil in the presence of clean hydrogen containing gas,
(ii) separating the effluent of step (i) into hydrotreated hydrocarbon oil and used hydrogen containing gas, which hydrotreated hydrocarbon oil is removed from the process,
(iii) hydrotreating fresh hydrocarbon oil in the presence of used hydrogen containing gas obtained in step (ii),
(iv) separating the effluent of step (iii) into partly hydrotreated hydrocarbon oil and contaminated hydrogen containing gas, which contaminated hydrogen containing gas is removed from the process, and
(v) transporting partly hydrotreated hydrocarbon oil obtained in step (iv) to step (i). Further, the invention relates to a reactor vessel suitable for carrying out such process.

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The present invention relates to a process for hydrotreating in a single reactor vessel comprising at least an upper and a lower catalyst bed a hydrocarbon oil which is substantially liquid at process conditions and to a reactor vessel suitable for carrying out such process.

It is foreseen that the amount of contaminating compounds, such as sulphur and aromatics, allowed to be present in hydrocarbon oils according to environmental legislation, will continuously decrease in the future. Therefore, there is much interest in processes with the help of which the content of such compounds in hydrocarbon oils can be reduced to a low level in a commercially attractive way.

In some catalytic desulphurization processes, such as described in e.g. British patent specification 1420248, use is made of two or more fixed-bed catalytic reaction systems, each consisting of one or more reaction vessels. The capital investment needed for such processes utilizing several reaction vessels, is higher than the capital investment needed for the present single reactor vessel process.

The present invention relates to a process for hydrotreating in a single reactor vessel comprising at least an upper and a lower catalyst bed, a hydrocarbon oil which is substantially liquid at process conditions, which process comprises:

(i) contacting partly hydrotreated hydrocarbon oil obtained in step (iv) described hereinbelow, at elevated temperature and pressure in the upper catalyst bed with a hydrotreating catalyst in the presence of clean hydrogen containing gas,

(ii) separating the effluent of step (i) into hydrotreated hydrocarbon oil and used hydrogen containing gas, which hydrotreated hydrocarbon oil is removed from the process,

(iii) contacting fresh hydrocarbon oil at elevated temperature and pressure with a hydrotreating catalyst in the lower catalyst bed in the presence of used hydrogen containing gas obtained in step (ii),

(iv) separating the effluent of step (iii) into partly hydrotreated hydrocarbon oil and contaminated hydrogen containing gas, which contaminated hydrogen containing gas is removed from the process, and

(v) transporting partly hydrotreated hydrocarbon oil obtained in step (iv) to step (i).

In the process according to the present invention, the final hydrotreating step is carried out in the presence of hydrogen which may contain a relatively small amount of hydrogen sulphide, which leads to good hydrotreating results.

The present hydrotreating process differs from conventional hydrotreating processes, such as described in US patent specification 4,243,519, in the sequence of the process steps. In the process according to the present invention the final hydrotreating step is carried out in the upper catalyst bed. Whereas, on the contrary, in the conventional process, the final hydrotreating step is carried out in a lower catalyst bed, which is situated further downstream the hydrogen gas flow. By operating the final hydrotreating step in the upper catalyst bed, one has the advantage of operating it at the highest hydrogen partial pressure maintained in the vessel, due to the pressure drop over the vessel. A higher hydrogen partial pressure gives better hydrotreating results.

Further, the use of a feedstock which is substantially liquid at process conditions makes that the separation of hydrocarbon oil and hydrogen containing gas can be attained without the need to cool down the partly hydrotreated oil, separate gas from liquid and to heat the partly hydrotreated oil up again, which is disadvantageous from an economical point of view.

It is now possible to obtain the same good results as in a countercurrent mode of operation without suffering from the inherent disadvantages of countercurrent operation, such as restrictions on the gas and liquid space velocity.

The present invention relates furthermore to a reactor vessel suitable for hydrotreating a hydrocarbon oil according to the invention, in which vessel:

(a) above the upper zone for retaining a catalyst bed is situated an inlet for gas and an inlet for liquid,

(b) between the upper and lower zones for retaining a catalyst bed is situated a separating means for separating liquid and gas,

(c) between the upper zone for retaining a catalyst bed and the separating means is situated an outlet for liquid,

(d) between the separating means and the lower zone for retaining a catalyst bed is situated an inlet for liquid,

(e) below the lower zone for retaining a catalyst bed is present an outlet for gas and an outlet for liquid, or an outlet for liquid and gas,

to which vessel a means is attached for transporting liquid obtained from the outlet for liquid situated below the lower zone for retaining a catalyst bed to the inlet for liquid situated above the upper zone for retaining a catalyst bed.

The process according to the present invention suitably comprises a hydrodesulphurization process in step (iii) followed by a further hydrodesulphurization process in step (i). In this way a very low sulphur level can be attained in a commercially attractive way. Other contaminants, such as nitrogen containing compounds, can also to a certain extent be removed in a hydrodesulphurization process. Further, the process suitably involves a hydrodesulphurization process in step (iii) followed by a hydrogenation process in step (i). In that way both the sulphur and the aromatics content of the fresh hydrocarbon oil can be diminished in a commercially attractive way.

The hydrocarbon oil subjected to the present process is substantially liquid at process conditions. The liquid phase of the hydrocarbon oil makes that the separation of the hydrotreated hydrocarbon oil from the hydrogen containing gas in step (ii) can be attained in a simple way. Suitably this separation is carried out with the help of one or more separating trays consisting of a conventional liquid draw-off tray as used in distillation units.

The separation of step (iv) can be carried out outside or inside the reactor vessel. In the first case, the hydrocarbon oil will usually be cooled down and needs heating up before it can be used in step (i). Therefore, separation inside the reactor, preferably with the help of a separating tray as described above, is preferred.

The pressure drop over the reactor vessel will generally be between 0.2 and 10 bar, more specifically between 0.5 and 5 bar. It is possible to add hydrogen to the lower catalyst bed. However, in general the hydrogen partial pressure will be higher in the upper catalyst bed than in the lower catalyst bed. The pressure drop will generally make that the hydrogen partial pressure in the upper catalyst bed is between 0.1 and 9 bar, more specifically between 0.4 and 4.5 bar higher than in the lower catalyst bed.

With the expression "clean hydrogen containing gas" is meant a gas containing less than 3% by volume of hydrogen sulphide, preferably less than 1% by volume, more preferably less than 0.5 % by volume, most preferably less than 0.1 % by volume. Suitably, contaminated hydrogen containing gas obtained in step (iv) is cleaned, e.g. by treating it with an amine, and subsequently used in step (i) as clean hydrogen containing gas.

A hydrocarbon oil which is substantially liquid at process conditions, is understood to comprise a hydrocarbon oil of which a major amount, for example more than 70 % by weight suitably more than 80 % by weight, and preferably more than 95 % by weight, is in the liquid phase. Hydrocarbon oils which can be suitably treated in the process according to the present invention, comprise any hydrocarbon which is substantially liquid at process conditions, for example kerosene fractions. A hydrocarbon oil which could be suitably treated in the process would be a gas oil, as the environmental constraints on this oil fraction have become quite strict. A suitable gas oil would be a gas oil substantially, e.g. more than 75% by weight, boiling in the range between 150 and 400 °C.

If a gas oil is hydrotreated in the process according to the present invention, steps (i) and (iii) are suitably carried out at a temperature of between 150 and 450 °C, suitably between 300 and 400 °C, preferably between 325 and 390 °C, more preferably between 340 and 385 °C, and step (i) is suitably carried out at a pressure of between 20 and 85 bar, preferably between 30 and 65 bar, and step (iii) is suitably carried out at a pressure of between 15 and 80 bar, preferably between 25 and 60 bar.

Further, in the present process suitably a lubricating oil can be hydrotreated, such as a lubricating oil substantially, e.g. more than 95% by weight, boiling in the range between 320 and 600 °C.

If a lubricating oil is hydrotreated in the process according to the present invention, steps (i) and (iii) are suitably carried out at a temperature of between 300 and 400 °C, preferably between 325 and 390 °C, more preferably between 340 and 385 °C, and a pressure of less than 250 bar, preferably less than 200 bar, more preferably less than 175 bar.

The hydrotreating catalyst employed in the process according to the present invention, suitably comprises one or more metals from Group 1b, 2a, 4b, 5b, 6b, 7b and 8 of the Periodic Table of the Elements in the Handbook of Chemistry and Physics, 63rd edition, on a solid carrier. The carrier can optionally comprise a zeolite.

As described above, the hydrotreating process according to the present invention preferably involves in step (i) a hydrogenation process and in step (iii) a hydrodesulphurization process, or in both steps a hydrodesulphurization process.

In the first mode, in step (i) a hydrogenation catalyst is applied at hydrogenation conditions which include a temperature of between 150 and 350 °C, and in step (iii) a hydrodesulphurization catalyst is applied at hydrodesulphurization conditions. In such case, the hydrodesulphurization of step (iii) must in general be carried out such that a sulphur content is attained which is such that the specification on the sulphur tolerance of the hydrogenation catalyst of step (i) is met, as otherwise this hydrogenation catalyst could be poisoned. Suitably, the hydrocarbon oil obtained in step (iv) contains not more than 15% by

volume of sulphur containing compounds, based on volume of sulphur containing compounds present in the fresh hydrocarbon oil, preferably not more than 10%.

In the second mode, in both step (i) and (iii) a hydrodesulphurization catalyst is applied at hydrodesulphurization conditions. In that case, the partly hydrotreated hydrocarbon oil obtained in step (iv) suitably contains between 1 and 30% by volume of sulphur containing compounds, based on volume of sulphur containing compounds present in the fresh hydrocarbon oil.

The present invention can suitably be carried out in a reactor vessel as shown in Figure 1.

The upper catalyst bed can contain either a hydrodesulphurization or a hydrogenation catalyst; the lower catalyst bed contains a hydrodesulphurization catalyst. Clean hydrogen containing gas is fed to the reactor via line 2, while partly hydrotreated hydrocarbon oil is introduced in the upper part of the reactor via line 1. The inlet for gas and the inlet for liquid can be combined. However, it is preferred to have separate inlets. The hydrotreated effluent from the upper catalyst bed is separated from gas with the help of a draw-off tray. The separated hydrotreated hydrocarbon effluent is removed from the reactor via line 3, while used hydrogen containing gas passes the separating tray and reaches the lower catalyst bed. Via line 4 fresh hydrocarbon oil is introduced between the separating tray and the lower catalyst bed. The partly hydrotreated effluent obtained after passing the fresh hydrocarbon oil over the lower catalyst bed, is removed from the reactor via line 5 and separated into partly hydrotreated hydrocarbon oil which is sent to line 1, and contaminated hydrogen containing gas. The contaminated hydrogen containing gas is suitably cleaned by treating it with an amine, so-called scrubbing. The cleaned gas obtained can then, optionally together with make-up hydrogen, be recycled to line 2 and be used again.

The advantages of the present invention will be illustrated by the following example.

EXAMPLE

The process was carried out in a set-up as described in Figure 1. The catalyst present both in the upper and the lower catalyst bed was a hydrodesulphurization catalyst, comprising 3.1% by weight of cobalt and 12.4% by weight of molybdenum, based on total amount of catalyst, on alumina. The catalyst particles were in the shape of 1.2 mm trilobes.

A gas oil feedstock of which according to the ASTM distillation curve more than 78% by volume is in the gaseous phase at 383 °C, more than 50% by volume is in the gaseous phase at 345 °C and more than 20% is in the gaseous phase at 300 °C was led to the reactor via line 4. The overall process conditions comprise a temperature of 360 °C and a weight hourly space velocity of 2.0 kg/l.h and a hydrogen to oil ratio of 200 Nl/kg. The hydrogen partial pressure at the outlet of the upper catalyst bed was 24.4 bar, while the hydrogen partial pressure at the outlet of the lower catalyst bed was 23.1 bar. At these process conditions about 7 % by weight of the gas oil feedstock was in the gaseous phase. The sulphur content of the feed, the partly hydrotreated feed and the hydrotreated feed are shown in Table 1, in amount of elemental sulphur on total amount of feed.

Table 1

	feed	partly hydrotreated feed	hydrotreated feed
Sulphur content (% by weight)	1.64	0.21	0.06

Not according to the invention, fresh feedstock as described hereinabove was processed in a set-up similar to the one of Figure 1, at process conditions substantially as described hereinabove. No intermittent hydrogen separation took place between the catalyst beds; no hydrocarbon oil was added or removed between the catalyst beds. The hydrogen partial pressure at the reactor outlet was 23.1 bar. The hydrotreated hydrocarbon oil obtained had a sulphur content of 0.11%wt.

Claims

1. Process for hydrotreating in a single reactor vessel comprising at least an upper and a lower catalyst bed, a hydrocarbon oil which is substantially liquid at process conditions, which process comprises:
   (i) contacting partly hydrotreated hydrocarbon oil obtained in step (iv) described hereinbelow, at elevated temperature and pressure in the upper catalyst bed with a hydrotreating catalyst in the presence of clean hydrogen containing gas,

(ii) separating the effluent of step (i) into hydrotreated hydrocarbon oil and used hydrogen containing gas, which hydrotreated hydrocarbon oil is removed from the process,

(iii) contacting fresh hydrocarbon oil at elevated temperature and pressure with a hydrotreating catalyst in the lower catalyst bed in the presence of used hydrogen containing gas obtained in step (ii),

(iv) separating the effluent of step (iii) into partly hydrotreated hydrocarbon oil and contaminated hydrogen containing gas, which contaminated hydrogen containing gas is removed from the process, and

(v) transporting partly hydrotreated hydrocarbon oil obtained in step (iv) to step (i).

2. Process according to claim 1, in which contaminated hydrogen containing gas obtained in step (iv) is cleaned and used in step (i).

3. Process according to claim 2, in which the contaminated hydrogen containing gas is cleaned by treating with an amine.

4. Process according to any one of claims 1-3, in which the clean hydrogen containing gas contains less than 3% by volume of hydrogen sulphide.

5. Process according to any one of claims 1-4, in which the hydrocarbon oil is a gas oil substantially boiling in the range between 150 and 400 °C.

6. Process according to claim 5, in which steps (i) and (iii) are carried out at a temperature of between 325 and 390 °C and step (i) is carried out at a pressure of between 20 and 85 bar, and step (iii) is carried out at a pressure of between 15 and 80 bar.

7. Process according to any one of claims 1-4, in which the hydrocarbon oil is a lubricating oil substantially boiling in the range between 320 and 600 °C.

8. Process according to claim 7, in which steps (i) and (iii) are carried out at a temperature of between 325 and 390 °C and a pressure of less than 200 bar.

9. Process according to any one of claims 1-8, in which the catalyst comprises one or more metals from Group 1b, 2a, 4b, 5b, 6b, 7b and 8 of the Periodic Table of the Elements, on a solid carrier.

10. Process according to any one of claims 1-9, in which in step (i) a hydrogenation catalyst is applied at hydrogenation conditions, and in step (iii) a hydrodesulphurization catalyst is applied at hydrodesulphurization conditions.

11. Process according to claim 10, in which the hydrocarbon oil obtained in step (iv) contains not more than 10% by volume of sulphur containing compounds, based on volume of sulphur containing compounds present in the fresh hydrocarbon oil.

12. Process according to any one of claims 1-9, wherein in step (i) and (iii) a hydrodesulphurization catalyst is applied at hydrodesulphurization conditions.

13. Process according to claim 12, in which the hydrocarbon oil obtained in step (iv) contains between 1 and 30% by volume of sulphur containing compounds, based on volume of sulphur containing compounds present in the fresh hydrocarbon oil.

14. Reactor vessel suitable for hydrotreating a hydrocarbon oil according to any one of claims 1-13, in which vessel:

(a) above the upper zone for retaining a catalyst bed is situated an inlet for gas and an inlet for liquid,

(b) between the upper and lower zone for retaining a catalyst bed is situated a separating means for separating liquid and gas,

(c) between the upper zone for retaining a catalyst bed and the separating means is situated an outlet for liquid,

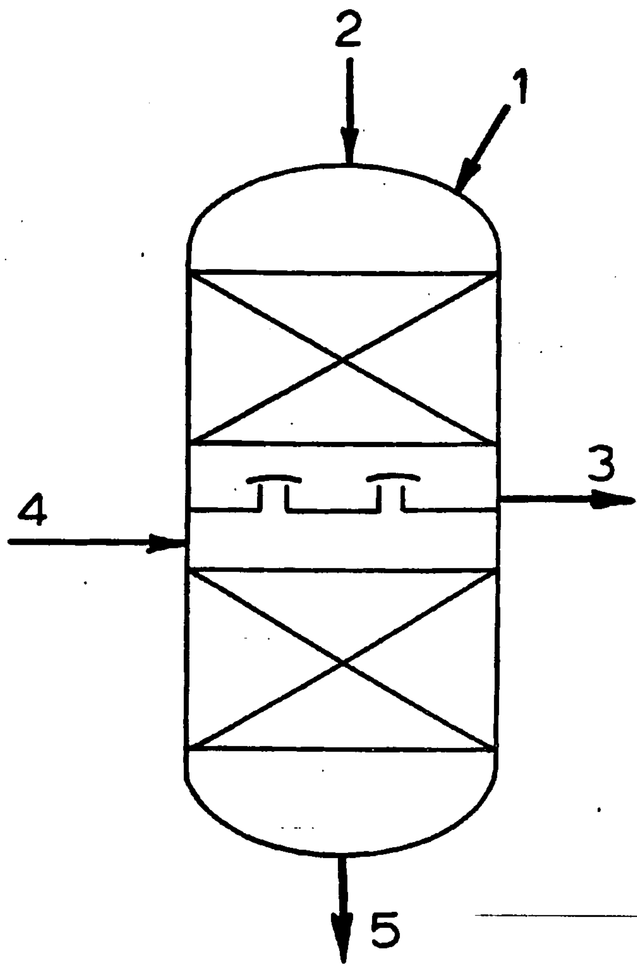
(d) between the separating means and the lower zone for retaining a catalyst bed is situated an inlet for liquid,

(e) below the lower zone for retaining a catalyst bed is present an outlet for gas and an outlet for liquid, or an outlet for liquid and gas,

to which vessel a means is attached for transporting liquid obtained from the outlet for liquid situated below the lower zone for retaining a catalyst bed to the inlet for liquid situated above the upper zone for retaining a catalyst bed.

15. Hydrocarbons obtained in a process as described in any one of claims 1-13.

FIG.1



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EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0165

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,A	US-A-4 243 519 (EXXON) * claims 1,2,3,4,9,11,12,13 * * column 2, line 64 - column 3, line 2 * * column 3, line 34 - line 37 * ---	1,2,4,9, 10,12, 13,15	C10G49/00 C10G65/04
A	US-A-2 971 900 (SOCONY MOBIL) * claims 1,4 * * column 7, line 15 - line 26 * * column 8, line 7 - line 24 * * figure 7 * ---	1,5,6,7, 8,9	
A	BE-A-755 268 (TEXACO) * claim 1 * * figure 1 * -----	1	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 MAY 1993	Oswald De Herdt

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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